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Influence of compositional deviations on the properties of $Cu_2ZnSnSe_4$ monograin powders

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Abstract

We have investigated the influence of compositional deviations on the properties of $Cu_2ZnSnSe_4$ (CZTSe) monograin powders in order to determine the optimal preparation conditions for CZTSe based photovoltaic solar cells. EDX results indicate that to obtain a single phase CZTSe powder the initial composition of precursors should be in the range of $0.83 < Cu/(Zn+Sn) < 1.0$. If $Cu/(Zn+Sn) \geq 1.0$ secondary phases were found by Raman investigations and identified as $SnSe_2$ and Cu_xSe. The CZTSe grain resistance increased with decreasing the ratio of Cu/(Zn+Sn) and increasing the ratio of Zn/Sn. The shape of as-grown CZTSe powder crystals depends mostly on the mass ratio of flux/CZTSe. All $Cu_2ZnSnSe_4$ (CZTSe) monograins exhibited *p*-type conductivity.

Keywords: $Cu_2ZnSnSe_4$; CZTSe; composition; Raman; morphology

1. Introduction

$Cu_2ZnSnSe_4$ (CZTSe) is a promising solar cell material due to it's direct bandgap around 1.04 eV, it's large absorption coefficient ($> 10^4$ cm^{-1}), and the cheap technology of it's production as all elemental components are abundant in the earth's crust [1].

In this study quaternary CZTSe is grown in monograin form. Powder technologies are one of the cheapest technologies for materials production and it is shown that the synthesis of CZTSe from initial binary compounds in the isothermal re-crystallization in different molten fluxes appears to be a relatively simple, inexpensive and convenient method to produce powder materials with very good crystal structure, homogeneity, and reduced concentration of inherent defects. The advantages of the developed powder

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materials are: (1) single-crystalline structure of every grain; (2) uniform distribution of doping impurities; (3) narrow granulometric composition [2, 3].

A prerequisite for high efficiency solar cells is the use of single phase materials, which according to the theoretical calculations is very demanding. The chemical potential region for stable single phases is very small [4]. It is important to note that up to now only few studies have been published on the phase diagram of Cu_2Se-ZnSe-$SnSe_2$ [5, 6].

Results of a previous study of the dependence of physical properties of $CuInSe_2$ monograin materials on the ratio of Cu/In [7] suggest that there is a need to also investigate the effect of different Cu/(Zn+Sn) and Zn/Sn ratios on the properties of CZTSe materials. These studies allow to determine the limits of compositional ratios for the growth of single phase CZTSe, and also to optimize the synthesis conditions for producing CZTSe materials with the desired properties. With this objective, we have carried out the current investigations. The present paper reports the effects of different compositional ratios on the properties of CZTSe monograin powders and identifies the optimum conditions to obtain high quality powders.

2. Experimental

In this study CZTSe powder materials with different compositions were synthesized from high- purity compounds (CuZnSn alloy, Cu-Se, ZnSe and SnSe) and elemental Se in the liquid phase of a flux material in evacuated quartz ampoules. The CuZnSn metal alloy and ZnSe binary compound precursors used for the CZTSe monograin synthesis were commercial compounds. CuSe and SnSe binary compounds were self-synthesized from high purity elements in evacuated quartz ampoules at temperatures of 773 and 1013 K, respectively. The latter precursors were grinded in an agate mortar before use in the powder growth process. As a flux material, water-soluble potassium iodide (KI) was used. The precursors were mixed in desired amounts and ratios, milled in a ball mill, degassed under dynamic vacuum, sealed into evacuated quartz ampoules and heated isothermally at 1013 K for 90 hours.

The formation of CZTSe monograin powders takes place during the heating process in the liquid phase of the flux. The latter must be used in an amount exceeding the limit for sintering of the initial precursor particles. The amount of the components for the CZTSe synthesis and the amount of flux were taken nearly equal to provide enough volume of the liquid phase for filling the free volume between the solid particles, which is one prerequisite for monograin growth. The formation of primary CZTSe particles begins after the melting of the flux material [8]. After the formation of the primary CZTSe particles the recrystallization starts. This thermodynamically-driven spontaneous process occurs because larger particles are energetically more favoured than smaller particles. The growth is stopped by quenching the synthesis ampoules to room temperature. The flux material is removed by leaching with deionized water and solid particles are washed by decantation. The released monograin powder is dried in a hot-air thermostat and sieved to narrow fractions from 20 µm to 112 µm.

The shape and surface morphology of the crystals were determined by high resolution scanning electron microscope (SEM). The chemical composition of the monograin powders was analyzed by energy dispersive x-ray spectroscopy (EDX). Room temperature (RT) Raman spectra were recorded by using a Horiba`s LabRam HR high resolution spectrometer equipped with a multichannel CCD detection system in backscattering configuration. The electrical resistance of the grains was determined by pressing the grain between two indium contacts. The ohmic behaviour of the contacts was proven by the linearity of the *I-V* curves. The conductivity type was determined by the hot-probe method.

3. Results and discussion

3.1. Analysis of elemental and phase composition

For the study of the influence of the Cu content in CZTSe, four powders were grown with different Cu content in precursors (21.6 mol% - 26.2 mol%) while the molar ratios of Zn/Sn = 1.03 and Se/Metal = 1.0 were kept constant. The composition of the monograin powders as molar ratios of Cu/(Zn+Sn) and Zn/Sn

are presented in Figure 1. It is seen that the molar ratio Cu/(Zn+Sn) of the product powders increases from 0.86 to 0.96 in the range of initial Cu/(Zn+Sn) values of 0.9 - 1.0. However, the ratio of Zn/Sn in the powders even decreases from 1.03 in to 0.98.

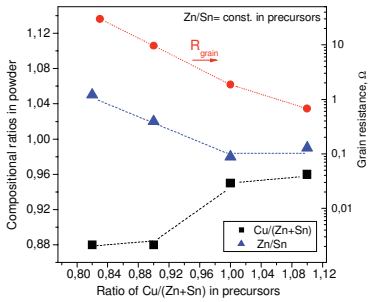

Fig. 1. Cu/(Zn+Sn) and Zn/Sn concentration ratios in powders and grain resistance as a function of Cu/(Zn+Sn) in precursors.

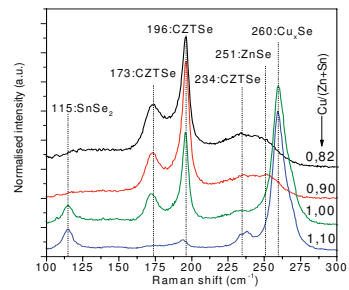

Fig. 2. RT Raman spectra of CZTSe with different Cu/(Zn+Sn) ratios in powders (Zn/Sn=1,03 and Se/Met=1).

RT Raman spectra of powder crystals (Fig. 2) revealed three main peaks at 196, 173 and 234 cm^{-1} which are characteristic for CZTSe [9]. In Cu-poor conditions (Cu/(Zn+Sn)) < 1.0), the presence of ZnSe at 251 cm^{-1} [10] as separate phase was detected. In the synthesis process part of the precursors and the formed material at growth temperature remains dissolved in the flux. During the cooling period the dissolved components precipitate from the flux and deposit on the surface of powder crystals. We suppose that very weak Raman modes of ZnSe originate from these deposits. In Cu-rich conditions (Cu/Zn+Sn) ≥ 1,0), Cu_xSe and $SnSe_2$ phases were detected at 260 cm^{-1} and 115 cm^{-1}, respectively [11, 12].

The results show that for single phase CZTSe powder growth starting with Zn/Sn = 1.03 the precursors ratio of Cu to other metals must be kept in the range of 0.83 < Cu/(Zn+Sn) < 1.0. Already in the case of Cu/(Zn+Sn) = 1.0, other phases become clearly detectable by Raman analysis.

The dependence of the CZTSe grain resistance on the Cu/(Zn+Sn) initial ratio is also shown in Fig.1 (right axis). The grain resistance decreases from 50 Ω to 0.4 Ω with increasing Cu/(Zn+Sn) ratio. All monograin powders exhibited *p*-type conductivity regardless of the Cu/(Zn+Sn) ratio. It can be concluded from these results that from Cu-rich precursors a semi-metallic Cu_xSe secondary phase is formed having a very low resistance and thereby preventing the use of the monograins for solar cells.

We also investigated a similar compositional dependence changing the Zn/Sn ratio in the precursors between 0.9 and 1.2, while the ratio of Cu/Sn = 1.85 was kept constant (Figure 3). However, Cu/(Zn+Sn) was changing from 0.83 to 0.96 in the previously found region of the single phase CZTSe. The results indicate that increasing the Zn content in the initial composition (Zn/Sn > 1.03) causes the decrease of the Cu content in the powders.

RT Raman spectra (Fig. 4) of powder crystals reveal three main peaks of CZTSe at 196, 173 and 234 cm^{-1}. Raman spectra of materials synthesized in Zn-rich conditions (Zn/Sn) ≥ 1.1), show existence of ZnSe as a secondary phase. In Zn-poor conditions (Zn/Sn) < 1.0 $SnSe_2$ phase emerges in addition to the ZnSe phase.

The results of this series using a constant ratio of Cu/Sn = 1.85 in the initial materials show that by adding excess of Zn (Zn/Sn = 1.03 - 1.1) the single phase region expands to the Cu-deficiency side. The resistances of CZTSe monograins with different Zn/Sn ratios are shown in Fig.3 on the right axis. All monograin powders in this series exhibited *p*-type conductivity regardless of Zn/Sn ratio. The grain resistance increased from 2 Ω to 234 Ω with increasing Zn/Sn ratio.

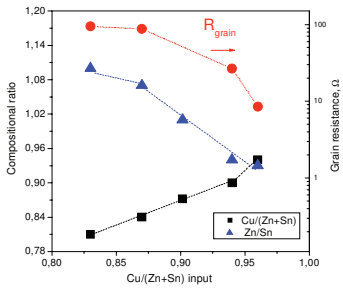

Fig. 3. Cu/(Zn+Sn) and Zn/Sn concentration ratios in powders and grain resistance as a function of Cu/(Zn+Sn) in precursors.

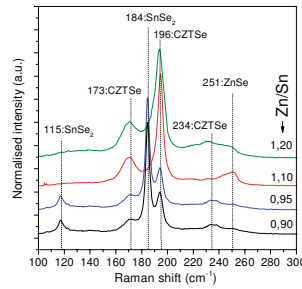

Fig. 4. RT Raman spectra of CZTSe with different Zn/Sn ratio in powders (Cu/Sn) = 1.85 and Se/Met = 1.03)

Summarising the results of both series of experiments we have shown that the composition of the powders can be tailored by changing both - the initial Cu and the Zn content taking into account that an increase of one of the component causes the decrease of the other at the same time.

Subsequently, we investigated monograin compositions when varying the ratio of Se/(Cu+Zn+Sn) in the precursors between 0.96 and 1.09 while the molar ratios of Cu/(Zn+Sn) and Zn/Sn were kept constant at 0.9 and 1.03 respectively. It can be concluded from the EDX and Raman studies that the bulk composition of the monograins did not change. However, a lack of chalcogen (Se/Met = 0.96) leads to the presence of additional Cu_xSe phases, which were not present in the case of excess of chalcogen (Se/Met = 1.03). At even higher Se/Met ratios (1.09) ZnSe and $SnSe_2$ phases were detected.

3.2. Morphology

In addition to the spectroscopic and electrical investigations also a morphological analysis of the referred set of materials was performed. SEM micrographs showed that the grown powder crystals had tetragonal shape with either sharp or rounded edges. It was found that there is no clear dependence of the shape of the crystals on the Cu/(Zn+Sn) or Zn/Sn ratio. However, the shape of the CZTSe powder crystals depends strongly on the volume ratio of flux to CZTSe (cm^3/cm^3), as can be seen in Figure 5. In the case of excess of flux (Flux/CZTSe > 1.6), the powder crystals had a tetragonal shape with very well formed crystal planes compared to powders grown in a lack of flux material (CZTSe/Flux < 0.54) which had rounded edges. In the case of a very low Flux/CZTSe value, there is not enough KI in the initial mix for monograins to grow undisturbed, thus the neighbouring monocrystals start to implicate each other hindering the formation of individual crystals. Also CuSe and Se from the initial precursors might start to act like flux material and the resulting material has more rounded edges due to much higher solubility of the material in CuSe-Se than in KI [8]. In the case of surplus KI, the monograins have more space to grow and therefore can obtain more regular-shaped planes and form tetragonal crystals. First results of a detailed EDX analysis of the powders grown after adding different amounts of Flux material indicate that in of the case of KI deficiency (CZTSe/KI = 0.4) powders with increased Cu/(Zn+Sn) and decreased Zn/Sn ratios are obtained. All the other CZTSe/KI ratios showed no significant changes in their compositional ratios.

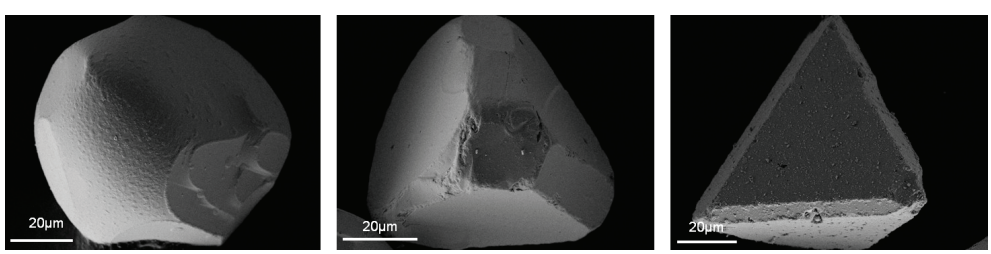

Fig. 5 SEM images of crystals grown with different ratio (cm^3/cm^3) of flux to CZTSe (a) 0.4, (b) 1.6 and (c) 4.9

4. Conclusions

$Cu_2ZnSnSe_4$ powders with various compositions were synthesised by isothermal crystallization method and the influence of the initial compositional ratios on the structural, morphological and electrical properties of CZTSe powders were investigated. The shape of CZTSe powder crystals depends mostly on the volume ratio of flux/CZTSe. Single-phase CZTSe monograins can be obtained in the range of 0,83 < Cu/(Zn+Sn) < 1.0 and Zn/Sn from 1.03 to 1.1. All other precursor compositions leads to the appearance of secondary phases, which are identified as ZnSe, $SnSe_2$ or Cu_xSe. All monograin powders exhibited *p*-type conductivity with resistance increasing from 0,4 Ω to 230 Ω with decreasing the ratio of Cu/(Zn+Sn) and increasing ratio of Zn/Sn.

Acknowledgements

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